

H...H Model Potential for Exchange–Repulsion Energy of Methane Dimer

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ABSTRACT: The procedure previously proposed for the parameterization of the exchange–repulsion energy using probe atom calculations is applied here to the study of the methane dimer and refined to give a very accurate anisotropic model potential in terms of atomic parameters. The most accurate model uses sites on C and H atoms and requires 12 parameters, but a description using just four isotropic sites shifted inward from the H atoms by 15% of the bond length is almost as accurate and is very simple in form. © 1998 John Wiley & Sons, Inc. *J Comput Chem* 19: 847–857, 1998

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Introduction

The development of very accurate general potentials for the calculation of interaction energies and properties of van der Waals complexes and for the classical molecular dynamics or Monte Carlo method prediction of properties of large assemblies of molecules is a continuing task. The force fields currently available for the calculation of intermolecular interactions are generally greatly

simplified and are suitable only for the type of system and property for which they were designed. Potentials designed for condensed phases cannot be applied to systems of a few molecules and vice versa. However, a sufficiently accurate force field which is designed to describe the interactions correctly, rather than by cancellation of errors, should be able to describe any property.

The determination of force field parameters is still largely done by adjusting them to reproduce experimental properties in the bulk. These data are usually not sufficient to determine all the non-bonding parameters. An alternative way of obtaining accurate model intermolecular potentials is by fitting to *ab initio* interaction energies.¹ In this way, a suitable analytical function, which depends on properties of the atoms (or better, atom pairs)

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belonging to the interacting molecules, is defined to reproduce the interaction energies for a set of van der Waals complexes. *Ab initio* methods provide a direct way to access the pair potential, in principle to a very high level of accuracy. Because the *ab initio* data refer to specific geometries of the interacting system, they provide much more useful information about the potential energy surface than experimental data, which generally involve extensive averaging over the geometrical parameters, and are better reserved for validation of the potentials and possibly for use in a final adjustment of a few critical parameters.

Two families of *ab initio* methods can be used in the calculation of intermolecular interaction energies. The most popular, the supermolecule method, has the advantage of being easy to apply once one is able to calculate energies and wave functions for isolated molecules, but it has the drawbacks of inherent inaccuracy arising from basis set superposition error (BSSE).² This problem is especially serious when the interaction energy of weakly bound complexes needs to be calculated and when electron correlation is important, as is the case in interactions dominated by dispersion.

The alternative is intermolecular perturbation theory (IMPT). The IMPT method of Hayes and Stone³ uses self-consistent field (SCF) unperturbed wavefunctions, and it is reasonably fast and quite accurate for repulsion energies.¹ The more recent symmetry adapted perturbation theory (SAPT) of Jeziorski and colleagues^{4,5} allows correlation effects to be taken into account and is very accurate, but it is still very costly in computational terms.

A particularly attractive feature of intermolecular perturbation theory is that it is partitioned into sums of contributions, arising from the corrections through different orders of the perturbation theory expansion. In most cases, these terms can be related to the long-range perturbation expressions of the interaction energy with well-defined physical meaning. The long-range expressions depend on properties of the isolated monomers and provide the most suitable analytical functions for representation of these terms.

Here, however, we are mainly concerned with the repulsive part of the interaction potential, which dominates at short intermolecular distances. Theory does not provide a simple analytical expression for the repulsion, but it has been found empirically that a good description can be obtained in terms of a sum of atom-atom terms that are exponentially decaying functions of the atom-atom distance. However, it is essential that these

atom-atom terms account correctly for the anisotropy of the repulsions, because atoms in molecules depart significantly from a spherical shape.

In the present study we sought a model for the repulsive interaction between methane molecules. Methane is an interesting molecule because it is generally believed to be close to spherical, but theoretical⁶⁻¹⁵ and experimental⁶⁻¹⁸ studies show that this is not the case. In particular, theoretical studies show that anisotropy is intrinsic to both the repulsive and the attractive contributions to the total interaction energy for the methane dimer. We address the question of whether the anisotropy in the repulsive part of the potential is due to the molecular shape or rather to the shapes of individual atoms in methane.

Moreover, it has recently been shown^{14,15} that different force fields give very different representations of the potential for the methane dimer, none of them accurate enough to account for the range of theoretical and experimental data available for this complex. Hill also pointed out the need for an anisotropic functional form for the methane intermolecular force field.¹⁵

Therefore, we wanted to find an accurate representation of the short-range potential for complexes involving methane. This is also a first step in determining accurate model potentials for complexes involving other hydrocarbons.

Method

An efficient, although not very accurate, way of dealing with atomic anisotropy when deriving pair potentials in the short range was proposed by Stone and Tong.¹⁹ In this method the anisotropic potential is derived by means of calculations with a probe atom. This method reduces the computational burden associated with any sampling of the multidimensional potential energy surface for the interaction between polyatomic molecules, provided that reliable methods exist for recovering the parameters for the interaction between two molecules from those for the interaction of each molecule with the probe.

The way to do this is by using so-called combining rules.²⁰ This procedure can give good results only if the probe atom bears some resemblance to the molecules of interest; therefore, the probe atom needs to be chosen carefully.

We applied the method of Stone and Tong¹⁹ to find a very accurate model for the short-range interaction potential of complexes involving methane. At this stage, the accuracy of the potential can only be tested by its ability to reproduce, in a least squares sense, the *ab initio* repulsion energies.

This method does not give very good results, as we shall see, and it needs to be refined further if very accurate potentials are required. This can be done by carrying out a number of calculations on the methane dimer itself and using these results to refine the parameters in the dimer potential. At this stage the general form of the repulsive potential has been found, and it is only necessary to adjust the parameters to obtain better agreement with the dimer calculations. This requires fewer of the expensive dimer calculations than would be needed to determine the form of the potential without the help of the probe calculations.

The details of the parameterization method were given in an earlier article.¹⁹ Only a general outline of the method is given here, together with specific features for its application to methane complexes.

The exchange–repulsion–penetration energy is recovered from the first-order energy as defined in the Hayes–Stone IMPT.³ The IMPT method is implemented in the CADPAC program.²¹

At first order the IMPT method takes into account the intermolecular electron exchange but not the electron correlation. The IMPT first-order interaction energy can be expressed as the sum of three contributions:

$$E_{\text{IMPT}}^{(1)} = E^{\text{ex}} + E^{\text{rep}} + E^{\text{es}}. \quad (1)$$

The electrostatic energy, E^{es} , in turn can be divided into two contributions: a long-range part, $E^{\text{es-lr}}$, arising from the multipolar expansion of the separated charge distributions of the monomers, and a short-range part $E^{\text{es-pen}}$, called electrostatic penetration, which corrects for the effects due to the overlap of the two charge distributions at medium and short range:

$$E^{\text{es}} = E^{\text{es-lr}} + E^{\text{es-pen}}. \quad (2)$$

The exchange (E^{ex}) and repulsion (E^{rep}) energies in eq. (1) and the electrostatic–penetration ($E^{\text{es-pen}}$) energy in eq. (2) show an $\exp(-R)$ behavior with respect to the interatomic distance R , and for this reason they can be added together to yield an exchange–penetration–repulsion energy of exponential form:

$$E^{\text{erp}} = E^{\text{ex}} + E^{\text{rep}} + E^{\text{es-pen}}. \quad (3)$$

The long-range contribution $E^{\text{es-lr}}$ to the electrostatic energy is calculated here via distributed multipole analysis (DMA)²² of the Hartree–Fock wave function for the monomers. The DMA method is also implemented in CADPAC.²¹ The short-range energy E^{erp} can then be calculated simply by subtracting this long-range term from the first-order energy:

$$E^{\text{erp}} = E_{\text{IMPT}}^{(1)} - E^{\text{es-lr}}. \quad (4)$$

In each case, the exchange–repulsion–penetration energy is fitted to the functional form

$$E^{\text{erp}} = C \sum_{ab}^{\text{pairs}} \exp[-\alpha^{ab}(\Omega)(R_{ab} - \rho^{ab}(\Omega))], \quad (5)$$

which was found in previous work to represent the exchange–repulsion–penetration energy accurately. In eq. (5), C is a dimensional constant, chosen to be 1 mH; ab denotes the interaction between atom (site) a on one of the monomers and atom b on the other; and $\Omega \equiv (\omega_a, \omega_b, \omega_{ab})$ is the set of orientational variables (Euler angles) that give the orientation of the local frames ω_a on atom a and ω_b on atom b , and the orientation ω_{ab} of the intersite vector, with respect to a global frame. R_{ab} is the distance between a and b (i.e., the length of the intersite vector).

The parameter α^{ab} is related to the steepness of the pair potential and can be regarded as describing the hardness of the site–site interaction. For any given orientation Ω , the parameter ρ^{ab} is equal to the distance between the atoms when the repulsive potential between those atoms is equal to C , so it can be regarded as describing the shapes of the atoms.¹⁹ The orientational dependence of α^{ab} and ρ^{ab} is expressed through linear combinations of the $\bar{S}_{l_a l_b}^{k_a k_b}(\Omega)$ rotational functions^{1,23}:

$$\alpha^{ab}(\Omega) = \sum_{l_a k_a l_b k_b l} \alpha_{l_a k_a, l_b k_b, l}^{ab} \bar{S}_{l_a l_b}^{k_a k_b}(\Omega), \quad (6)$$

$$\rho^{ab}(\Omega) = \sum_{l_a k_a l_b k_b l} \rho_{l_a k_a, l_b k_b, l}^{ab} \bar{S}_{l_a l_b}^{k_a k_b}(\Omega). \quad (7)$$

The parameters to be fitted are the coefficients of the \bar{S} functions in the linear combinations. The \bar{S} functions have definite symmetry, so many of the coefficients are zero by symmetry; moreover, the deviation of the sites from spherical symmetry is usually quite small, so the linear combinations converge rapidly. The potential in eq. (5) can be evaluated using the Orient program.²⁴

The \bar{S} functions with $l_b = 0$ must have $l = l_a$ and are spherical harmonics $C_{l_a k_a}(\theta_a, \varphi_a)$, where θ_a and φ_a are the polar angles of the intersite vector in the local axis system of site a . If site b is spherically symmetric, these are the only functions that occur. Similarly if site a is spherically symmetric, the only functions needed are the \bar{S} functions with $l_a = 0$, which are spherical harmonics $C_{l_b k_b}(\theta_b, \varphi_b)$ involving the polar angles of the intersite vector in the local axis system of site b . When both sites are nearly spherical, it is a good approximation to write

$$\rho^{ab} = \rho^{a(b)}(\theta_a, \varphi_a) + \rho^{b(a)}(\theta_b, \varphi_b), \quad (8)$$

where

$$\begin{aligned} \rho^{a(b)}(\theta_a, \varphi_a) &= \sum_{l_a k_a} \rho_{l_a k_a}^{a(b)} C_{l_a k_a}(\theta_a, \varphi_a), \\ \rho^{b(a)}(\theta_b, \varphi_b) &= \sum_{l_b k_b} \rho_{l_b k_b}^{b(a)} C_{l_b k_b}(\theta_b, \varphi_b); \end{aligned} \quad (9)$$

and similarly for α ,

$$\alpha^{ab} = \alpha^{a(b)}(\theta_a, \varphi_a) + \alpha^{b(a)}(\theta_b, \varphi_b), \quad (10)$$

where

$$\begin{aligned} \alpha^{a(b)}(\theta_a, \varphi_a) &= \sum_{l_a k_a} \alpha_{l_a k_a}^{a(b)} C_{l_a k_a}(\theta_a, \varphi_a), \\ \alpha^{b(a)}(\theta_b, \varphi_b) &= \sum_{l_b k_b} \alpha_{l_b k_b}^{b(a)} C_{l_b k_b}(\theta_b, \varphi_b). \end{aligned} \quad (11)$$

Equation (8) expresses ρ^{ab} as a sum of $\rho^{a(b)}$ and $\rho^{b(a)}$, which may be interpreted as describing the shapes of sites a and b , respectively. The notation $\rho^{a(b)}$ implies that the effective shape of site a may depend on the site with which it interacts. We might hope that to a good approximation it would be independent of the other site, so that

$$\rho^{a(b)}(\theta_a, \varphi_a) = \rho^{a(c)}(\theta_a, \varphi_a) = \rho^a(\theta_a, \varphi_a), \quad (12)$$

but we shall see that this is not the case for methane.

The general expression for ρ can be expressed in a form related to eq. (8):

$$\begin{aligned} \rho^{ab} &= \rho^{a(b)}(\theta_a, \varphi_a) + \rho^{b(a)}(\theta_b, \varphi_b) \\ &+ \sum_{l_a \neq 0} \sum_{l_b \neq 0} \sum_{k_a k_b l} \rho_{l_a k_a, l_b k_b, l}^{ab} \bar{S}_{l_a l_b l}^{k_a k_b}, \end{aligned} \quad (13)$$

with $\rho^{a(b)}$ and $\rho^{b(a)}$ given by eq. (9) as before. This formulation separates the terms $\rho^{a(b)}$ and $\rho^{b(a)}$, which describe the shapes of sites a and b , respec-

tively, from the remaining terms, which depend on both sites.

RELATIONSHIPS BETWEEN PARAMETERS

The parameters describing α and ρ for the methane-methane interaction are obtained initially from those for methane-neon by means of combining rules, although they are subsequently refined. The energy dependent hard core model²⁵ has been used as the combining rule. This performs better than other possible rules in a number of cases.¹⁹ According to this model, the α and ρ site-site parameters for the exchange-repulsion-penetration potential between two polyatomic molecules in terms of those for the complexes between each molecule and the probe atom are

$$1/\alpha^{ab} = 1/\alpha^{ap} + 1/\alpha^{bp} - 1/\alpha^{pp}, \quad (14)$$

$$\rho^{ab} = \rho^{ap} + \rho^{bp} - \rho^{pp}. \quad (15)$$

These rules imply combining rules relating α^{ab} to α^{aa} and α^{bb} ,

$$\frac{1}{\alpha^{ab}} = \frac{1}{2} \left(\frac{1}{\alpha^{aa}} + \frac{1}{\alpha^{bb}} \right), \quad (16)$$

and relating ρ^{ab} to ρ^{aa} and ρ^{bb} ,

$$\rho^{ab} = \frac{1}{2}(\rho^{aa} + \rho^{bb}). \quad (17)$$

The last of these relationships implies eq. (8), together with transferability [i.e., that $\rho^{a(b)}$ is independent of b , eq. (12)].

Because the combining rule for the α parameter is not linear, it leads to a somewhat more complicated expression for the anisotropic components of α . If we assume that the anisotropy in α is small, so that eqs. (10) and (11) can be used, the combining rule (14) leads to the following expression for the anisotropic components of site a :

$$\alpha_{lk}^{a(b)} = \left(\frac{\alpha_{00,00}^{ab}}{\alpha_{00,00}^{ap}} \right)^2 \alpha_{lk,00}^{ap}. \quad (18)$$

It follows that the anisotropic components $\alpha_{lk}^{a(b)}$ are not the same for all sites b , but that

$$\frac{\alpha_{lk}^{a(b)}}{\alpha_{lk}^{a(c)}} = \left(\frac{\alpha_{00,00}^{ab}}{\alpha_{00,00}^{ac}} \right)^2. \quad (19)$$

Like (12), this relationship is expected to apply approximately rather than exactly in practice.

COMPUTATIONAL DETAILS

A neon atom was used to probe the repulsive wall for methane. Hill showed¹⁵ that this probe is optimal for the purpose of recovering the potential for complexes involving methane because it is isoelectronic with methane and it gives results similar to those obtained with a N atom, a well-established probe for molecules made up of first row atoms. For the probe calculation we require E^{erp} for the neon dimer and for the $\text{Ne} \cdots \text{CH}_4$ complex. Here the long-range electrostatic energy is zero, so $E^{\text{erp}} = E_{\text{IMPT}}^{(1)}$.

For all the calculations the 6-311++G(2d,2p) basis set was used. The CH_4 geometry was optimized at the SCF level and the optimized C—H bond length is 2.044 bohr.

In each case, a range of intermolecular distances was chosen so that the $E_{\text{IMPT}}^{(1)}$ values fell in the range 0.5–8.0 mH.

For the $\text{Ne} \cdots \text{Ne}$ complex 12 energy values were calculated for Ne–Ne distances in the range from 4.0 to 7.0 bohr.

The IMPT first-order energies for the $\text{Ne} \cdots \text{CH}_4$ complex were calculated for 18 symmetry distinct positions (R, θ, φ) of the Ne atom relative to the methane molecule; this corresponds to 268 configurations when symmetry is taken into account. The configurations span distances R in the range between 5.0 and 7.0 bohr and angles (θ, φ) chosen to cover the sphere uniformly.

In the case of the CH_4 dimer, IMPT first-order energies were calculated for 54 configurations characterized by C \cdots C intermolecular distances ranging from 6.0 to 9.0 bohr. The $\text{CH}_4 \cdots \text{CH}_4$ configurations most studied in previous work were represented in this set, including the one identified as the absolute energy minimum.^{6–8}

The distributed multipole moments and the pair repulsion parameters are defined with respect to local atomic frames for methane. The local frame for the C atom is chosen with the z axis along one of the C—H bonds and the x axis in the plane containing another C—H bond. (Because of the symmetry it does not matter which bonds are chosen.) The local z axis for each H atom is taken along its C—H bond and the local x axis in the plane containing another C—H bond. With this choice of axes, all the H atoms carry the same multipole moments and the same pair parameters for the model short-range energy, and their local symmetry is fully exploited.

A weighted least squares fitting procedure has been adopted throughout. The weighting scheme

is Boltzmann-like, and the Boltzmann factor is taken as 2.5 mH.

Results

Ne \cdots Ne

The isotropic parameters recovered from the $\text{Ne} \cdots \text{Ne}$ dimer repulsion energy fitting are

$$\alpha_{00,00}^{\text{NeNe}} = 2.469 \text{ bohr}^{-1},$$

$$\rho_{00,00}^{\text{NeNe}} = 4.868 \text{ bohr}.$$

The Boltzmann-weighted root mean square (RMS) error of the fit is 6.3 μH .

Ne \cdots CH₄

For the $\text{Ne} \cdots \text{CH}_4$ repulsion energies three fitting schemes are used. For two of them, repulsion parameters are assigned either to the C atom only (C-site model) or to the H atoms only (H-site model). For the third, repulsion parameters are assigned to all atoms (five-site model).

C-Site Model

Table I shows the results for several models in which the repulsion is fitted with a single site at the C atom. We have not listed the actual parameter values, but they are available from the authors by anonymous ftp.²⁶

An isotropic model (C0 in Table I) gives a poor result; the weighted RMS of the residuals is 413 μH , or about 1 kJ mol^{−1}, which may be compared with the well depth at the equilibrium geometry of about −0.463 kJ mol^{−1} for a spherical model potential¹⁷ and −0.381 kJ mol^{−1} as determined from a BSSE corrected supermolecule calculation.¹⁴

TABLE I.
Fitted Models for $\text{Ne} \cdots \text{CH}_4$ Complex: C \cdots Ne
Pair Repulsion Only.

Model	Parameters ^a	ΔE (μH)
C0	$\alpha_{00}^{\text{C}}, \rho_{00}^{\text{C}}$	413
C1	$\alpha_{00}^{\text{C}}, \rho_{00}^{\text{C}}, (\rho_{30}^{\text{C}}, \rho_{33c}^{\text{C}}),$ $(\rho_{40}^{\text{C}}, \rho_{43c}^{\text{C}})$	33
C2	$\alpha_{00}^{\text{C}}, (\alpha_{30}^{\text{C}}, \alpha_{33c}^{\text{C}}), (\alpha_{40}^{\text{C}}, \alpha_{43c}^{\text{C}}), \rho_{00}^{\text{C}},$ $(\rho_{30}^{\text{C}}, \rho_{33c}^{\text{C}}), (\rho_{40}^{\text{C}}, \rho_{43c}^{\text{C}})$	29

^aParameters not mentioned (e.g., $\rho_{10}^{\text{C}}, \rho_{11s}^{\text{C}}$, etc.) are zero because of symmetry. Pairs of parameters enclosed in parentheses [e.g., $(\rho_{30}^{\text{C}}, \rho_{33c}^{\text{C}})$] are related to each other by symmetry.

Better results are obtained with a model potential that has some angular dependence, for example, model C1. The lowest rank nonspherical terms in ρ are ρ_{30}^C and ρ_{33c}^C ; but because of symmetry $\rho_{30}^C = \sqrt{5}/2\rho_{33c}^C$, and they represent only one independent fitting parameter. Similarly ρ_{40}^C and ρ_{43c}^C are symmetry related: $2\sqrt{5}\rho_{40}^C = -\sqrt{7}\rho_{43c}^C$. Consequently model C1 has only two more independent parameters than model C0, but these allow the RMS error in the fit to be reduced by more than an order of magnitude. Allowing the hardness parameter α to be anisotropic (model C2) does not lead to a significant improvement, and neither does the addition of further anisotropic terms in ρ .

H-Site Model

The carbon atom in methane is shielded from repulsive interactions by the hydrogen atoms that surround it, and we may expect that any repulsion due to the carbon atom can be represented by a modification of the H atom repulsions. Accordingly, we investigated models in which the H atoms alone contribute to the repulsion (Table II). This gives much better results than the C-centered repulsion without a significant increase in the number of fitting parameters.

Model H0, in which the H atoms are treated as isotropic, is not very good; but inclusion of just one additional parameter to describe the anisotropy of the H atom (model H1) improves the fit by an order of magnitude to 12 μ H. Increasing the num-

ber of ρ parameters further (model H2) gives a modest improvement, but it does not justify the substantial number of additional parameters. Note that because the site symmetry at the H atoms is C_{3v} , not T_d as at the C atom, there is no symmetry relationship between ρ_{30}^H and ρ_{33c}^H ; so model H2 has 10 independent parameters.

A more effective way to improve the description is to allow α to be anisotropic as well as ρ . Model H3, with five parameters in all, including $\alpha_{10,00}^H$, has an RMS error of 5 μ H; this can be reduced to 2 μ H by including $\rho_{30,00}^H$ and $\rho_{33c,00}^H$ (model H4). In fact the value of $\rho_{20,00}^H$ in this model is very small, and it can be dropped without affecting the error (model H5).

Five-Site Model

The five-site model with isotropic parameters (model CH0 in Table III) gives a much smaller r.m.s. error than the models with isotropic sites on C only or H only. However it requires 4 parameters, and is not better than C-site or H-site models with a comparable number of parameters.

Better fits are obtained by allowing α and ρ for the C atom to be anisotropic (model CH1), ρ to be anisotropic on both C and H (model CH2), or by a combination of these (model CH3). In every case, however, the quality of fit is no better for a given number of parameters than can be obtained using repulsion on H atoms only.

TABLE II.
Fitted Models for Ne...CH₄ Complex: H...Ne Pair Repulsion Only.

Model	Parameters	ΔE (μ H)
H0	$\alpha_{00}^H, \rho_{00}^H$	153
H1	$\alpha_{00}^H, \rho_{00}^H, \rho_{10}^H$	12
H2	$\alpha_{00}^H, \rho_{00}^H, \rho_{10}^H, \rho_{20}^H, \rho_{30}^H, \rho_{33c}^H, \rho_{40}^H, \rho_{43c}^H, \rho_{50}^H, \rho_{53c}^H$	4
H3	$\alpha_{00}^H, \alpha_{10}^H, \rho_{00}^H, \rho_{10}^H, \rho_{20}^H$	5
H4	$\alpha_{00}^H, \alpha_{10}^H, \rho_{00}^H, \rho_{10}^H, \rho_{20}^H, \rho_{30}^H, \rho_{33c}^H$	2
H5	$\alpha_{00}^H, \alpha_{10}^H, \rho_{00}^H, \rho_{10}^H, \rho_{30}^H, \rho_{33c}^H$	2

CH₄...CH₄ REPULSION

The Ne...CH₄ results can now be used with the help of combining rules to give an initial estimate of the potential between two methane molecules. For this we use the two most successful models of the Ne...CH₄ repulsion: models H5 and CH3. From the H5 model, using the energy-dependent hard-core combining rule described above, we obtain a methane-methane repulsion model based on H...H repulsions only. The CH3 model leads in a similar way to a repulsion model

TABLE III.
Fitted Models for Ne...CH₄ Complex: C...Ne and H...Ne Pair Repulsion.

Model	Parameters	ΔE (μ H)
CH0	$\alpha_{00}^C, \rho_{00}^C$	31
CH1	$\alpha_{00}^C, \alpha_{30}^C, \alpha_{33c}^C, \rho_{00}^C, \rho_{30}^C, \rho_{33c}^C$	11
CH2	$\alpha_{00}^C, \rho_{00}^C, \rho_{30}^C, \rho_{33c}^C, \alpha_{00}^H, \rho_{00}^H$	6
CH3	$\alpha_{00}^C, \alpha_{30}^C, \alpha_{33c}^C, \rho_{00}^C, \rho_{30}^C, \rho_{33c}^C, \alpha_{00}^H, \rho_{00}^H, \rho_{10}^H$	2

that contains C...C and C...H repulsions, as well as H...H repulsions. We have not attempted to construct a single-site repulsion model based on the models in Table I, because the errors in those models suggest that the results would not be very good.

The two parameter sets in Table IV have been tested for their ability to reproduce the IMPT exchange-repulsion-penetration energy for different configurations of the CH₄ dimer. The quality of models is estimated in two ways, following the procedure described by Stone and Tong.¹⁹ The value Δ*E* tabulated is the RMS of the difference between the IMPT energy and the energy calculated using the model for the same dimer geometry. To calculate Δ*R* we proceed as follows. We calculate the IMPT energy *E*^{erp}(*R*, Ω) at a particular geometry (*R*, Ω). The energy given by the model will usually be different. We vary the center of mass separation *R* of the dimer, but not the relative orientation Ω, until the energy *E*(*R*', Ω) calculated by the model matches the IMPT energy *E*^{erp}(*R*, Ω) at the original separation. The difference *R* - *R*' is a measure of the error of the model in describing the position of the repulsive wall, and the value Δ*R* shown in Table IV is the RMS of these differences.

We see that the error Δ*E* is in the 0.4–0.6 mH (1.0–1.5 kJ mol⁻¹) region, while Δ*R* is about 0.2–0.3 bohr. The IMPT exchange-repulsion-penetration energy at the equilibrium geometry of the methane dimer is about 1.7 kJ mol⁻¹, so these errors are quite unacceptable. Nevertheless, these models provide a good starting point for further refinement, and it is worth explaining why it is helpful to proceed in this way rather than by fitting a methane dimer repulsion potential directly to dimer data.

Consider the CH₃ model for methane dimer; the parameters are listed in Table IV. It has 12 independent parameters, in principle, although in the combining-rule formulation its parameters are derived from the seven parameters of the CH₃

Ne...CH₄ model and the two parameters of the Ne...Ne model. If one attempts to improve the fit to the IMPT dimer energies by direct optimization, one finds that there are strong correlations between these 12 parameters; in an unconstrained optimization some of them rapidly take on physically impossible values. Direct optimization of such a 12-parameter model is therefore impossible without imposing constraints (e.g., by fixing some of the parameter values), but if one is starting from scratch it is very difficult to know what values to choose.

The probe-atom/combining-rule procedure however gives sensible values for all of the parameters, making it a straightforward matter to fix some of them and optimize the rest. Analysis of the uncertainties using singular value decomposition shows that some of the parameter values have large uncertainties, and it is these parameters that tend to take on unreasonable values if allowed to vary freely. Where the uncertainty in a parameter is large compared with its value, the value can be set to zero without affecting the quality of the fit significantly; otherwise it can be fixed at the value provided by the probe-atom/combining-rule procedure, again without affecting the quality of the fit very much.

A more general approach is to impose linear constraints on the parameter values. As noted above, the parameters ρ₃₀^C and ρ_{33c}^C must satisfy the symmetry relationship ρ₃₀^C = √5/2 ρ_{33c}^C, and similarly 2√5 ρ₄₀^C = -√7 ρ_{43c}^C. These constraints are essential: without them the potential would not have the correct symmetry. It would be possible to achieve the same result by replicating the fitted points on the potential energy surface so that they formed a completely symmetrical array in the orientational space. However, this would involve increasing the number of points very substantially and it is a clumsy approach.

A second type of constraint follows from the combining rules (14) and (15). In this case, however, the relationship is not exact and may not

TABLE IV.
Combining-Rule Models for CH₄...CH₄ Complex.

Model	Parameters	Δ <i>E</i> (μH)	Δ <i>R</i> (bohr)
CH3	α ₀₀ ^{C(C)} , (α ₃₀ ^{C(C)} , α _{33c} ^{C(C)}), ρ ₀₀ ^{C(C)} , (ρ ₃₀ ^{C(C)} , ρ _{33c} ^{C(C)}), α ₀₀ ^{H(C)} , (α ₃₀ ^{C(H)} , α _{33c} ^{C(H)}), ρ ₀₀ ^{H(C)} , ρ ₁₀ ^{H(C)} , (ρ ₃₀ ^{C(H)} , ρ _{33c} ^{C(H)}), α ₀₀ ^{H(H)} , ρ ₀₀ ^{H(H)} , ρ ₁₀ ^{H(H)}	585	0.33
H5	α ₀₀ ^H , α ₁₀ ^H , ρ ₀₀ ^H , ρ ₁₀ ^H , ρ ₃₀ ^H , ρ _{33c} ^H	411	0.22

even be approximately correct because it depends on the validity of the combining rules. Consequently, much milder constraints are appropriate than for the symmetry relationships and they should be removed altogether in the final stages of the fit, if this is possible without the parameters drifting away to unreasonable values.

Further constraints are suggested by the transferability approximation. For ρ this implies that $\rho^{a(b)}$ is independent of b , and for α it is expressed by (19). Here too the relationships are not expected to hold exactly, so the constraints should be mild.

These constraints can all be imposed by adding penalty functions to the sum of squares of residuals, each of the form

$$K(c_0 + c_1 p_1 + c_2 p_2 + \cdots)^2,$$
(20)

where $(c_1 p_1 + c_2 p_2 + \cdots)$ is a linear combination of parameters p_i that should be equal to $-c_0$ (usually zero) if the constraint is satisfied. The constant K is adjustable. A large value of K is used for a symmetry constraint, and a smaller value gives a milder constraint.

Using this approach we optimized the parameters of the CH3 model. Four particular cases are of interest. They differ in the constraints that are used; the symmetry constraints are applied in all cases because it would be meaningless to relax them.

1. If all constraints suggested by the combining rules and the transferability approximation are applied, the weighted RMS residual is 31.1 μ H. The parameter values are listed in Table V, fit *a*; values of parameters that are related to one or more other parameters by constraints are shown in parentheses.
2. If the combining-rule constraints on the isotropic components of ρ and α are removed but the transferability constraints remain, the parameter values change significantly but the RMS residual hardly changes.
3. If the transferability constraints are removed but the combining-rule constraints remain, the RMS residual falls to 12.3 μ H. The parameters for this case are shown in Table V, fit *b*.
4. If all but the symmetry constraints are removed, the RMS residual falls to 11.9 μ H, and the parameters change to the values are given in Table V, fit *c*.

These results show that the combining-rule constraints on the isotropic components of ρ and α

TABLE V.
Fitted Five-Site Models with Constraints for
CH₄ ⋯ CH₄ Complex.

Pair	CC	CH	HH
Fit a: 7 independent parameters, $\Delta E_{rms} = 31.1 \mu\text{H}$			
$\alpha_{00,00}$	2.170	(1.880)	1.837
$\alpha_{30,00}$	0.107	(0.080)	
$\alpha_{33c,00}$	(0.095)	(0.072)	
$\rho_{00,00}$	5.543	(5.028)	4.514
$\rho_{00,10}$		−0.221	(−0.221)
$\rho_{30,00}$	0.264	(0.264)	
$\rho_{33c,00}$	(0.236)	(0.236)	
Fit b: 10 independent parameters, $\Delta E_{rms} = 12.3 \mu\text{H}$			
$\alpha_{00,00}$	1.947	(1.894)	1.843
$\alpha_{30,00}$	0.070	−0.225	
$\alpha_{33c,00}$	(0.062)	(−0.201)	
$\rho_{00,00}$	5.713	(5.088)	4.463
$\rho_{00,10}$		−0.220	−0.222
$\rho_{30,00}$	−0.100	0.360	
$\rho_{33c,00}$	(−0.090)	(0.322)	
Fit c: 12 independent parameters, $\Delta E_{rms} = 11.9 \mu\text{H}$			
$\alpha_{00,00}$	2.288	1.867	1.848
$\alpha_{30,00}$	0.284	−0.185	
$\alpha_{33c,00}$	(0.254)	(−0.166)	
$\rho_{00,00}$	5.515	5.172	4.425
$\rho_{00,10}$		−0.248	−0.209
$\rho_{30,00}$	−0.128	0.336	
$\rho_{33c,00}$	(−0.115)	(0.300)	

Parameters with values given in parentheses are related to other parameters by one or more constraints. See the Results section for details.

can be imposed without making the fit significantly worse. This means that these parameters are not very well determined individually by the fitting procedure. However, the imposition of the transferability constraints does make the fit worse, and Table V shows that when the constraint is relaxed the parameter values are very far from satisfying eqs. (12) and (19). Indeed, the CC and CH parameters that are equal when the constraints are applied turn out to have opposite signs when the constraint is relaxed. We have to conclude either that the simple classical picture of ρ as describing the shape of an atom is seriously misleading or that for some reason it does not work for this particular example. One possible reason is that the C atom here is almost completely shielded by the H atoms, so that there is no orientation of the molecules where the C–C interaction domi-

nates. Consequently the C-C part of the model in this case is not very well defined and may be describing rather different aspects of the potential from those that the simple classical picture attributes to it.

Problems of this kind do not arise for the H-site models because there is only one kind of site and none of these relationships between parameters can apply, so it is not necessary to impose any constraints to arrive at a satisfactory fit.

The H-site model H5 improves substantially on further optimization to a value of 37 μH for ΔE (Table VI). A small additional improvement is obtained by adding terms in \bar{S}_{110}^{00} (to give model H5+ in Table VI) and \bar{S}_{112}^{00} (to give model H5++). The improvement does not however justify the additional parameters, even though the extra terms are not complicated to evaluate.

The most remarkable result is obtained for the H1 H-site model, which yields an RMS error of 40 μH , or 0.1 kJ mol^{-1} , with only three parameters. The combining rule parameter values are in this case quite close to the adjusted values (Table VII), but the changes are significant. The table shows an estimate of the uncertainty in the fitted parameters, given quite arbitrarily as the change in the parameter that increases the RMS error by 25%, and it is evident that these uncertainties are generally considerably smaller than the differences between the combining-rule values and the fitted ones.

The form of ρ for this model is

$$\rho^{\text{H(H)}} = \rho_{00} + \rho_{10} \cos \theta, \quad (21)$$

where θ is the angle between the direction of the C-H bond and the intersite vector. When ρ_{10}/ρ_{00} is small, this describes a circular contour shifted by ρ_{10} in the direction corresponding to $\theta = 0$. Consequently, an equivalent description is obtained by shifting the H sites outward by ρ_{10} . In fact, the optimized value of ρ_{10} is -0.304 bohr, so we need to shift the H sites inward by 0.304 bohr. This then gives a four-site model H'0 with only

TABLE VI.
H-Site Fitted Models for $\text{CH}_4 \cdots \text{CH}_4$ Complex.

Model	Parameters	ΔE (μH)
H1	$\alpha_{00}^{\text{H}}, \rho_{00}^{\text{H}}, \rho_{10}^{\text{H}}$	40
H5	$\alpha_{00}^{\text{H}}, \alpha_{10}^{\text{H}}, \rho_{00}^{\text{H}}, \rho_{10}^{\text{H}}, r_{30}^{\text{H}}, \rho_{33c}^{\text{H}}$	37
H1+	$\alpha_0^{\text{H}}, \rho_{00}^{\text{H}}, \rho_{10}^{\text{H}}, \rho_{10,10,0}^{\text{HH}}$	33
H1++	$\alpha_{00}^{\text{H}}, \alpha_{10}^{\text{H}}, \rho_{00}^{\text{H}}, \rho_{10}^{\text{H}}, \rho_{10,10,0}^{\text{HH}}, \rho_{10,10,2}^{\text{HH}}$	27

TABLE VII.
Comparison between Combining Rule Parameters and Their Optimized Values for Model H1 in Table V.

Parameter	Comb. rule value	Optimized value
$\alpha_{00,00}^{\text{HH}} \text{ bohr}^{-1}$	1.729	1.855 (35)
$\rho_{00,00}^{\text{HH}} \text{ bohr}$	4.958	4.794 (10)
$\rho_{10,00}^{\text{HH}} \text{ bohr}$	-0.354	-0.304 (12)

Parameter values are in atomic units; an estimate of the uncertainty in the least significant digit is given in parentheses.

two parameters (although the site position may be viewed as a third parameter), and its RMS error is only 34 μH . The optimized parameters for this model are $\rho_{00}^{\text{H}'} = 4.805$ bohr and $\alpha_{00}^{\text{H}'} = 1.857$ bohr $^{-1}$. This is a very much simpler model than any model using C sites as well as H, and is preferable to the more elaborate models, even though the fit to the *ab initio* results is not quite as good.

Lii and Allinger²⁷ proposed a similar model for describing repulsion-dispersion in hydrocarbons as part of the MM3 force field. They used repulsion-dispersion sites shifted inward from the H atoms by 7.7% of the C-H bond length. For the CH_4 dimer, Tsuzuki et al.¹² used a Buckingham-type potential²⁸ with five interaction sites for the nonbonding interactions (repulsive and attractive), four of them at positions shifted inward from the H atom positions by 13% of the C-H bond length. It was quite successful, although the minimum was too shallow. Schindler et al.¹¹ used a model potential for the CH_4 dimer and for the $\text{CH}_4 \cdots \text{N}_2$ complex in which the distance of the H interaction site from the C atom was an adjustable parameter (with an optimal value of about 83% of the C-H bond length), corresponding to a 17% shift of the H site toward the C atom. We found that the RMS error ΔE for a model four-site exchange-repulsion-penetration potential with purely isotropic parameters is minimized when the sites are shifted inward from the H atom by $\sim 15\%$ of the bond length.

SAPT Calculations

Having established the general form of the repulsion potential, we carried out a number of calculations using the SAPT program of Jezierski

et al.⁵ with the same $6-311++G(2d,2p)$ basis set as was used for the IMPT calculations. We used 16 symmetrical geometries for the dimer (seven orientations at two or three distances each) and 20 random geometries chosen by rotating each molecule through a random angle about a randomly chosen axis; for these the distance was chosen randomly in the range of 5–10 bohr. The first-order energies were calculated; and correlation corrections were calculated to second order, including response terms. In the notation of Jeziorski et al.⁵ the interaction terms were $E_{\text{pol}}^{(10)} + E_{\text{exch}}^{(10)}$, together with the correlation corrections $E_{\text{pol,resp}}^{(12)} + E_{\text{exch}}^{(11)} + E_{\text{exch}}^{(12)}$. The results were fitted to a model with four isotropic repulsion sites on the C—H bond (1.732 bohr from the C atom) and with distributed multipoles at these sites and at the C atom. The multipoles were calculated using the Brueckner double-excitation method,²¹ also using the same basis set; this level of calculation is appropriate when SAPT is used, because the interaction energy includes coupled-cluster correlation corrections to second order. MP2 multipoles were also calculated and were very similar. The results are shown in Table VIII with the results of the isotropic four-site fit to the IMPT results for comparison. Once again estimates of the uncertainties in the fitted parameters are given as the changes that would increase the RMS error by 25%. It is evident that the repulsion parameters are almost identical and that the fit is rather better, which is a very encouraging result because it suggests that the much cheaper IMPT calculations should give reliable results for repulsion energies in larger systems where SAPT cannot be used.

Conclusions

We found that the atom-probe procedure for finding the interaction energy between pairs of molecules is useful in exploring suitable functional

forms for the interaction potential, but the fit to the true dimer potential is not very good and has to be refined with the help of calculations on the dimer. However, fewer of the expensive dimer calculations are needed when the probe calculation was carried out to identify the form of the potential.

A further advantage of the probe-atom procedure is that a general repulsion potential for the dimer contains many parameters that are strongly correlated with each other. In such a situation it is difficult to justify constraining the parameters without additional information about the nature of the constraints to be applied. The probe-atom procedure provides such information; and because the molecule-probe system is simpler, it is less affected by correlations between parameters and provides suitable starting values for the parameters.

For the particular case of methane, we explored a variety of models for the repulsion with varying degrees of atomic anisotropy. Previous workers pointed out that H atom sites are needed for an accurate analytical fit to the potential energy surface.⁸ The most accurate model that we found for the exchange–repulsion–penetration energy (with an RMS error of 12 μH when compared with *ab initio* dimer calculations) uses sites on C and H atoms and requires 12 parameters; but a much simpler model uses only four sites at positions shifted inward from the H atoms by 15% of the bond length and needs only two parameters, each of the four sites being isotropic. The RMS error for this potential is 36 μH , which is larger than for the more elaborate potential; but for most purposes the greater error will be outweighed by the simplicity of the model.

We also carried out some calculations using the SAPT of Jeziorski et al.,⁵ which uses coupled-cluster theory to calculate correlation corrections to the interaction energy. The repulsion energy from these calculations was fitted to a similar isotropic four-site model. We found that the parameters were almost identical, and the RMS difference between the model and the SAPT energies was only 24 μH . The close agreement between the IMPT and SAPT models is very encouraging for work on larger systems where the SAPT method is currently too expensive in computer time, because it implies that the much cheaper IMPT method should give reliable results.

Work is in progress to find the remaining terms in the potential for methane dimer. We expect that the repulsion potential for methane should be

TABLE VIII.
Parameter Values for Isotropic Four-Site Models.

	C–X distance (bohr)	$\alpha_{00,00}^{\text{H}}$ (bohr ^{−1})	$\rho_{00,00}^{\text{H}}$ (bohr)	rms error (μH)
IMPT	1.730	1.871 (40)	4.818 (10)	34
SAPT	1.732	1.861 (30)	4.836 (9)	24

Values are in atomic units. An estimate of the uncertainty in the least significant digit is given in parentheses.

transferable to other hydrocarbons, and this is also under investigation.

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